Organometallic Chemistry

Synthesis of clusters $Fe_2(CO)_6(\mu\text{-}XCH_2CH{=}CH_2)(\mu_3\text{-}X)Fe(CO)_2Cp$ (X = Se, S; Cp = η^5-C_5H_5)

S. N. Konchenko, V. A. Maksakov, I. Yu. Filippov, and V. A. Varnek*

Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3 prosp. Acad. Lavrent'eva, 630090 Novosibirsk.
Fax: 007 (383 2) 35 5960

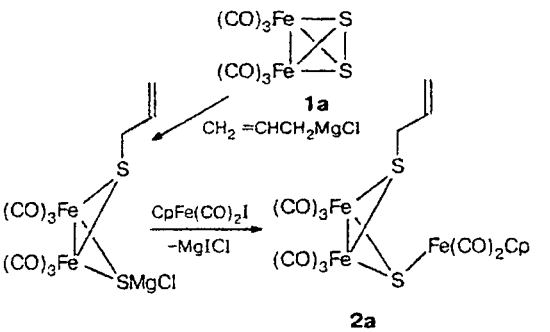
The clusters $Fe_2(CO)_6(\mu\text{-}XCH_2CH{=}CH_2)(\mu_3\text{-}X)Fe(CO)_2Cp$ (X = S, Se) were prepared by the successive treatment of the bi- and trimetallic complexes $Fe_2(CO)_6(\mu\text{-}Se_2)$ and $Fe_3(CO)_9(\mu_3\text{-}X)$ with allylmagnesium chloride and $CpFe(CO)_2I$. The clusters obtained contain a noncoordinated C=C bond. The structure of the Se-containing cluster was suggested on the basis of comparison of its spectral data (IR, ^1H NMR, and Mössbauer spectra) with the spectra of the analogous S-containing complex, which was previously characterized by X-ray diffraction analysis.

Key words: carbonyl clusters, cluster monomers, iron, sulfur, selenium, synthesis.

Interest in cluster compounds of transition metals containing ligands with free olefin substituents is caused by the possibility of their copolymerization with traditional organic monomers.[1] This method for preparing metal-immobilized polymeric materials has been previously used for a series of $Os_3(CO)_{12}$ derivatives[2] obtained by the coordination of unsaturated ligands on clusters containing the Os_3-metallocycle.[3] Recently, we have suggested another approach to preparing "cluster monomers" (Scheme 1).[4]

In this case, along with the addition of an unsaturated radical to the coordinated ligand, the skeleton of a new cluster is formed during the synthesis, which makes it possible to vary the composition and structure of the obtained compounds more extensively. In terms of this approach, one may plan the development of "homologous" series of clusters. For this purpose, complexes containing not only S, but Se and Te as well, and at the second stage of the synthesis, electrophilic complexes of other transition metals, can be used as the starting reagents.

Scheme 1



2a

The present work is devoted to applying this synthetic approach to Se-containing iron carbonyl derivatives.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1371—1374, July, 1997.

1066-5285/97/4607-1317 $18.00

Results and Discussion

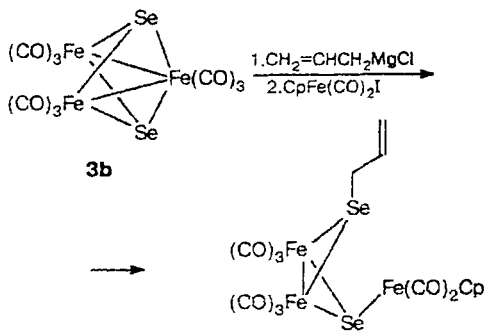
The complex $Fe_2(CO)_6(\mu\text{-}S_2)$ (**1a**) is one of the most widely used synthons for directed synthesis of both homo- and heterometallic sulfur-containing carbonyl iron-based clusters by assembly from fragments of lower nuclearity.[5,6] Interest in this compound is due in many respects to the existence of the bridged S_2-fragment, which manifests several properties typical of organic dichalcogenides.[6] The reaction of **1a** with allylmagnesium chloride can be an example. In this reaction, the S—S bond is cleaved, and a complex with pronounced nucleophilic properties, which can replace the iodide ligand in $CpFe(CO)_2I$,[4] is formed (Scheme 1). The product of this reaction, cluster $Fe_2(CO)_6(\mu_3\text{-}SCH_2CH{=}CH_2)(\mu_3\text{-}S)Fe(CO)_2Cp$ (**2a**), can be obtained by the same scheme when the trimetallic cluster $Fe_3(CO)_9(\mu_3\text{-}S)_2$ (**3a**) is used instead of **1a**. However, the yield of **2a** is substantially lower, and the procedure of its isolation is more difficult. The use of **3a** can be considered to be not promising because convenient methods for the one-step preparation of **1a** from accessible reagents, $Fe(CO)_5$ and sodium polysulfide, are known.[7]

The chemistry of $Fe_2(CO)_6(\mu\text{-}Se_2)$ (**1b**) is much more poorly studied than that of its analog, **1a**,[8] and the most convenient method for its preparation is the reaction of $Fe_3(CO)_9(\mu_3\text{-}Se)_2$ (**3b**) [9] with bases in polar solvents resulting in the fragmentation of **3b** and the formation of a bimetallic complex. Taking this into account, for the synthesis of the Se-containing analog of **2a**, we used both complexes **1b** and **3b** as the starting reagents.

The successive addition of allylmagnesium chloride and $CpFe(CO)_2I$ to **1b** and treatment of the reaction mixture, as in the case of S-containing derivatives[4] (see Scheme 1), results, in fact, in the formation of the cluster $Fe_2(CO)_6(\mu_3\text{-}SeCH_2CH{=}CH_2)(\mu_3\text{-}Se)Fe(CO)_2Cp$ (**2b**).

Cluster **3b** can also be used as the starting reagent, but in this case, the formation of **2b** is observed only when the reaction mixture is heated to 60 °C after the addition of $CpFe(CO)_2I$ (Scheme 2).

Scheme 2



Unlike in the case of S-containing analogs, the use of **3b** for the preparation of **2b** is fairly promising, because the total yield of the final product calculated per initial $Fe(CO)_5$ is higher than when **1b** is used, since the stage of preparation of **1b** from **3b** is ruled out.

In order to determine the structure of **2b**, several of its spectral parameters were compared with the corresponding data for **2a**, whose structure was previously determined by X-ray diffraction analysis.[4] The IR spectrum of **2b** in the carbonyl region almost repeats the spectrum of **2a**. The main difference is a small shift of the absorption bands to lower frequencies (Table 1). As in the case of **2a**, the ^1H NMR spectrum of compound **2b** contains a singlet signal of protons of the cyclopentadienyl ligand and three signals more, two complicated multiplets (protons of the —CH= and $=CH_2$ groups) and a doublet ($—CH_2—$), which are typical of an allyl fragment that does not participate in the coordination with the metal. Replacement of the chalcogen has a slight effect on the chemical shifts of the corresponding signals (Table 1).

The Mössbauer spectrum of **2b**, like that of **2a**, is a superposition of two quadrupole doublets with a ratio of intensities of ~2 : 1 (Table 1, Fig. 1), which agrees with the structure of molecule **2b** presented in Scheme 2. The difference in the δ values for the corresponding doublets in the spectra of **2b** and **2a** can be understood on the basis of the theory of partial chemical shifts: when sulfur is replaced with selenium, an increase in δ should be expected because in the series of ligands, sulfur-containing ligands have the minimum partial shift.[10]

Table 1. IR, ^1H NMR, and Mössbauer (MBS) spectral data for clusters **2a** and **2b**

Compound	IR (νCO/cm^{-1})	^1H NMR, (δ, J/Hz)	MBS (δ/mm s^{-1} (ε))[a]
2a	2062m, 2034v.s, 2025s, 1995m, 1990s, 1977s, 1970m, 1959w	3.02 (d, 2 H, $—CH_2—$, J = 6.6) 4.95 (s, 5 H, C_5H_5) 5.04 (m, 2 H, $CH_2=$) 5.93 (m, 1 H, —CH=)	−0.05[b] (0.82) 0.09 (1.62)[c]
2b	2059m, 2039w, 2030v.s, 2024s, 1994m, 1988s, 1976s, 1968m, 1956w	3.16 (d, 2 H, $—CH_2—$, J = 6.6) 4.96 (s, 5 H, C_5H_5) 5.05 (m, 2 H, $CH_2=$) 5.99 (m, 1 H,—CH=)	−0.03 (0.86)[b] 0.12 (1.73)[c]

[a] Measurement errors $\delta(\varepsilon)$ are equal to 0.01 mm s^{-1} (0.02).
[b] Doublet of greater intensity belongs to 2 Fe.
[c] Doublet of smaller intensity belongs to 1 Fe.

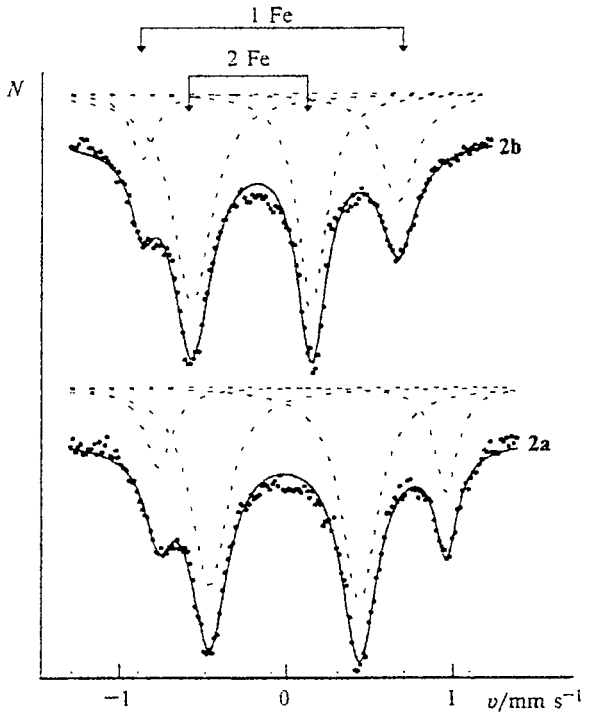


Fig. 1. Mössbauer spectra of clusters **2a** and **2b**.

These spectral data allow us to conclude that the structure of the obtained compound **2b** is similar to that of **2a**.

Theoretically, complexes similar to **2a** and **2b** can be transformed into clusters with a closed metallocycle when one or several ligands are removed from their molecule. In the case of carbonyl derivatives, thermal or photochemical treatment of compounds is usually used for this purpose.[5] Based on thermogravimetric analysis, it was established that both compounds melt without decomposition. Mass losses of 52.5 and 58% occur in the 100—154 °C (**2a**) and 120—162 °C (**2b**) ranges, respectively, which suggests that the cluster decomposes completely without formation of intermediate products. An attempt to perform thermolysis not in the solid phase, but in solution, also did not result in the formation of new cluster products. Prolonged heating of solutions of both **2a** and **2b** in cyclohexane results in the formation of an amorphous precipitate, whose IR spectrum contains no signals in the carbonyl region. The solutions contain only one component: the initial compound. The electronic absorption spectra of **2a** and **2b** contain absorption bands with maxima at λ 530 and 536 nm, respectively. Therefore, for the photochemical initiation of closing of the metallocycle, solutions of these compounds in cyclohexane were irradiated by a mercury lamp in a Pyrex flask used as the light filter. The result was the same as in the case of the thermal treatment. It may be that the failures to close the metallocycle are reasonable and are related to specific features of the geometry of the molecules of these compounds. For example, it was established for **2a** that the μ-S—$CH_2CH{=}CH_2$ and —$Fe(CO)_2Cp$ groups are located on one side of the plane of $Fe_2(\mu_3\text{-}S)$.[4] This apparently impedes the convergence of the iron atoms to a distance sufficient for the formation of a bond.

Experimental

IR spectra of solutions in hexane were recorded on a Specord IR-75 spectrometer. ^1H NMR spectra were recorded on a Bruker SXP-4-100 spectrometer (90 MHz) in $CDCl_3$ relative to tetramethylsilane. Mössbauer spectra were recorded on an NP-610 spectrometer (^{57}Co in Pd as the source; standard α-Fe; ~20 °C). Electronic absorption spectra of solutions were recorded on a Specord M40 spectrophotometer. Thermogravimetric analysis was carried out on a Paulik—Paulik—Erdey derivatograph in an atmosphere of helium with a heating rate of 5 deg/min. Solvents were purified by distillation over the corresponding drying agents.[11] The starting compounds $Fe_3(CO)_9(\mu_3\text{-}S)_2$,[7] $Fe_2(CO)_6(\mu\text{-}S_2)$,[7] $Fe_3(CO)_9(\mu_3\text{-}Se)_2$,[9,12] $Fe_2(CO)_6(\mu\text{-}Se_2)$,[9,12] $CpFe(CO)_2I$,[13] and $CH_2{=}CH—CH_2MgCl$[13] were obtained by known procedures. All procedures were carried out in Schlenk glassware in an argon atmosphere (except for chromatography, which was carried out in air).

Synthesis of $Fe_2(CO)_6(\mu\text{-}SCH_2CH{=}CH_2)(\mu_3\text{-}S)$—$Fe(CO)_2Cp$ (2a) from $Fe_3(CO)_9(\mu_3\text{-}S)_2$ (3a). Solutions of $CH_2{=}CHCH_2MgCl$ (1.02 mmol) in THF (10 mL) and $CpFe(CO)_2I$ (0.277 g, 0.92 mmol) in THF (10 mL) were successively added to a solution of **3a** (0.442 g, 0.92 mmol) in THF (50 mL) at −78 °C. After slow heating to ~20 °C, the mixture was stirred for 1 h more. The precipitate that formed was filtered off, and the solvent was evaporated *in vacuo* to dryness. The solid residue was extracted with toluene (40 mL) at 80 °C. The extract was chromatographed on a column with silica gel using a hexane—benzene (1 : 1) mixture as the eluent. Unreacted **3a** (0.242 g) and **2a** (0.025 g, 11% with respect to reacted **3a**), which was identified by the IR spectrum,[4] were isolated.

Synthesis of $Fe_2(CO)_6(\mu\text{-}SeCH_2CH{=}CH_2)(\mu_3\text{-}Se)$—$Fe(CO)_2Cp$ (2b). ***A.* From $Fe_2(CO)_6(\mu\text{-}Se_2)$ (1b).** Solutions of $CH_2{=}CHCH_2MgCl$ (1.01 mmol) in THF (10 mL) and $CpFe(CO)_2I$ (0.320 g, 1.04 mmol) in THF (10 mL) were successively added to a solution of **1b** (0.456 g, 1.04 mmol) in THF (40 mL) at −78 °C. After slow heating to ~20 °C in a Dewar flask, the mixture was stirred for 30 min more. The white precipitate of magnesium halide that formed was filtered off, and the brownish-red solution was evaporated *in vacuo* to dryness. The solid residue was extracted with hot hexane. After cooling of the extract to −10 °C, the crystalline product with m.p. 84—85 °C was obtained in a yield of 0.170 g (25%).

***B.* From $Fe_3(CO)_9(\mu_3\text{-}Se)_2$ (3b).** Solutions of $CH_2{=}CHCH_2MgCl$ (0.7 mmol) in THF (10 mL) and $CpFe(CO)_2I$ (0.277 g, 1.38 mmol) in THF (10 mL) were successively added to a solution of **3b** (0.400 g, 0.69 mmol) in THF (40 mL) at −78 °C. After slow heating to ~20 °C and stirring for 1 h, the mixture was kept at 60 °C for 15 min. The precipitate was filtered off, and the solution was evaporated *in vacuo* to dryness. The solid residue was chromatographed on a column with silica gel using a hexane—benzene (1 : 1) mixture as the eluent. Unreacted **3b** (0.076 g) and **2b** (0.075 g, 20% with respect to reacted **3b**) were isolated.

References

1. A. D. Pomogailo and V. S. Savost'yanov, *Metallsoderzhashchie monomery and polimery na ikh osnove [Metal-Containing Monomers and Polymers Based on Them]*, Khimiya, Moscow, 1988 (in Russian).
2. N. M. Bravaya, A. D. Pomogailo, V. A. Maksakov, V. P. Kirin, T. I. Solov'eva, and P. I. Belov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 423 [*Russ. Chem. Bull.*, 1994, **43**, (Engl. Transl.).
3. V. A. Maksakov, V. P. Kirin, S. N. Konchenko, N. M. Bravaya, A. D. Pomogailo, A. V. Virovets, N. V. Podberezskaya, I. G. Barakovskaya, and S. V. Tkachev, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1293 [*Russ. Chem. Bull.*, 1993, **42**, (Engl. Transl.).
4. S. N. Konchenko, A. V. Virovets, V. A. Maksakov, I. Yu. Filippov, and N. V. Podberezskaya, *Mendeleev Commun.*, 1992, 165.
5. *Comprehensive Organometallic Chemistry*, Ed. G. Wilkinson, New York, 1982, **6**, 767.
6. K. H. Whitmire, *J. Coord. Chem.*, 1988, **17**, 95.
7. D. Seyferth, R. Hinderson, and L.-C. Song, *Organometallics*, 1982, **1**, 125.
8. L. C. Roof and J. W. Kolis, *Chem. Rew.*, 1993, **93**, 1037.
9. D. A. Lesch and T. B. Rauchfuss, *Inorg. Chem.*, 1981, **20**, 3583.
10. *Khimicheskie primeneniya messbauerovskoi spektroskopii [Chemical Application of Mössbauer Spectroscopy]*, Ed. V. I. Gol'danskii, Mir, Moscow, 1970 (in Russian).
11. A. J. Gordon and R. A. Ford, *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*, J. Wiley and Sons, New York, 1972.
12. L. F.Duhl and P. W. Sutton, *Inorg. Chem.*, 1963, **2**, 1067.
13. *Handbuch der präparativen anorganischen Chemie*, **6**, Ed. G. Brauer, Ferdinand Enke Verlag, Stuttgart, 1975.

Received February 10, 1997